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COMPOSITION COMPRISING AN ELASTOMERIC POLYMER AND AN OLEFINIC POLYMER@

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COMPOSITION COMPRISING AN ELASTOMERIC POLYMER AND AN OLEFINIC POLYMER.

5

The invention relates to a composition comprising an elastomeric polymer and an olefinic polymer, a preblend comprising the elastomeric polymer and the olefinic polymer and an extrusion process for the composition.

Compositions comprising an elastomeric polymer, for example an ethylene-propylene elastomeric polymer and polyethylene or polypropylene are known. It is said that such a composition shows a good kneading behaviour and that cost reduction is obtained.

A disadvantage of the known composition however is that it shows a low strain release, especially if the strain is applied at a temperature above room temperature. This becomes evident for example during the processing of the composition into shaped objects. If the composition is extruded into profiles or hoses, frequently during the production process a strain is applied to such profiles or hoses, for example when the profiles or hoses are bended along their longitudinal axis by the take-off unit of the processing line for the profile or hose. After releasing the stress that was put on the product advantageously also the strain is released so that the product takes back its original and intended shape.

However in the known composition the strain is released very slowly or sometimes not at all, so that the product does not come back into its intended shape and it is difficult to further process the product or to use the product in its application.

Surprisingly we found that this problem is solved, if the composition comprises:

- A. 100 parts by weight elastomeric polymer, comprising monomeric units of ethylene and an α -olefin,
- B. 1-50 parts by weight olefinic polymer, comprising:
 - b1. 98 - 65 weight % monomeric units of ethylene
 - b2. 2 - 35 weight % monomeric units of an alpha-olefin having 4 - 12 carbon atoms.

It is possible that the elastomeric polymer (A) is obtained by the polymerisation of ethylene and an α -olefin, so that it essentially consists of monomeric units of ethylene and the α -olefin (EPM). As α -olefin an α -olefin with 3 - 10 carbon atoms can for instance be used; examples are propene, butene, hexene, octene etc. Preferably, propene is used

Preferably as the elastomeric polymer (A) a polymer is used

comprising monomeric units of ethene, an α -olefin and a non-conjugated polyene (EPDM).

As α -olefin is used for instance an α -olefin with 3 - 10 carbon atoms; examples are propene, butene, hexene, octene etc. Preferably, propene is used.

5 The ethene to α -olefin weight ratio in elastomeric polymer (A) may be between 90/10 and 20/80. Preferably, the ethene to α -olefin weight ratio is between 70/30 and 40/60, more preferably the weight ratio is in between 60/40 and 40/60.

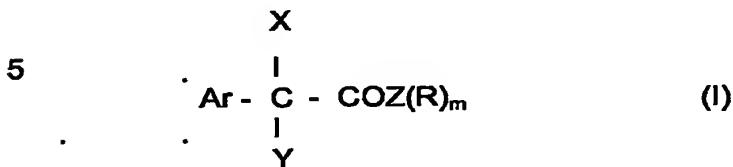
10 Examples of non-conjugated polyenes to be applied in the elastomeric polymer (A) are 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, 1,4 hexadiene or mixtures thereof. Preferably the elastomeric polymer (A) comprises 5-ethylidene-2-norbornene. The non-conjugated polyene may be present in the elastomeric polymer in amounts of 3-35 weight %, preferably 4-15 weight %. The preparation of elastomeric polymer (A) is known to the person skilled in the art. The polymer can for instance be prepared by polymerization with the help of a
15 Ziegler-Natta catalyst or a metallocene catalyst.

Preferably an elastomeric polymer (A) is used having a crystallinity of at most 5%, measured by means of DSC (differential scanning calorimetry), at room temperature and higher temperatures. Room temperature is defined as being 23 °C. Preferably the copolymer has a crystallinity of at most 1%, more preferably the
20 copolymer has no crystallinity above 23 °C. Even more preferably, the copolymer has no crystallinity above 0 °C. The crystallinity is determined from a DSC experiment, in which a polymer sample is heated at a rate of 20 °C/minute to 200 °C, is kept at that temperature for 5 minutes and is cooled down to -70 °C at a rate of 5 °C/minute. The thermal effects that than occur are recorded. The %-crystallinity is calculated from the
25 crystallisation enthalpy (ΔH , J/g sample) according to the formula:

$$\text{%-crystallinity} = \Delta H / 2.94. \quad (\text{XI})$$

Very good results are obtained if an elastomeric polymer (A) is used
30 comprising monomer units of a) ethylene, b) an α -olefin, c) a non-conjugated polyene (C) which in the molecule contains one C=C bond that is polymerizable using a Ziegler-Natta catalyst, and d) optionally a non-conjugated polyene (D) which in the molecule contains two or more C=C bonds, that are polymerizable using a Ziegler-Natta catalyst, which elastomeric polymer (A) is obtainable by a process wherein it is polymerized by
35 means of a catalyst composition comprising a Group 3, 4, 5 or 6 transition metal

compound and a Group 1, 2, 12 or 13 organometallic compound and a compound represented by the formula:



10 where:

X = a halogen atom,

Y = H, an alkyl group with 1-30 C atoms, an aromatic group with 6-30 C atoms, or a halogen atom,

$Z =$ O (oxygen) or N (nitrogen),

15 R independently represents H, an alkyl group with 1-30 C atoms or an aromatic group with 6-30 C atoms,

Ar = an aromatic group with 6-30 C atoms

$$m = 1 \text{ or } 2.$$

Such process is described in more detail in WO-98/00369.

Good examples of polyenes (C) are 5-ethylidene-2-norbornene and 1,4 hexadiene. Good examples of polyenes (D) are 5-vinyl-2-norbornene and dicyclopentadiene.

The polyene (C) may be present in an amount of 3 - 30 weight %, preferably 4 - 15 weight %. The polyene (D) may be present in an amount of 0,1 - 5 weight %, preferably 0,2 - 2 weight %.

A very suitable compound according to from. I is the ethyl ester of monochlorodiphenyl acetic acid.

The transition metal compound used in the catalyst composition preferably is VCl_4 , VCl_3 , $VCl_3 \cdot 3THF$ (with THF being a tetrahydrofuran group). The organometallic compound preferably is triethyl aluminium, triisobutyl aluminium, trioctyl aluminium, diethyl aluminium ethoxide, diisobutyl aluminium chloride, dimethyl aluminium chloride, diethyl aluminium chloride, methyl aluminium dichloride, ethyl aluminium dichloride, isobutyl aluminium dichloride, isobutyl aluminium sesquichloride, or ethyl aluminium sesquichloride. Most preferably the organometallic compound is diethyl aluminium chloride and ethyl aluminium sesquichloride.

The olefinic polymer (B) preferably comprises as monomeric units of the α -olefin, monomeric units of butene, hexene or octene. Most preferably the olefinic polymer (B) comprises monomeric units of ethylene and octene.

5 The olefinic polymer (B) preferably comprises 95 - 70 weight % monomeric units of ethylene and 5 - 30 weight % monomeric units of the α -olefin, more preferably the olefinic polymer (B) comprises 90 - 75 weight % monomeric units of ethylene and 10 - 25 weight % monomeric units of the α -olefin.

10 The olefinic polymer (B) may have a density of 880 - 915 kilograms per cubic meter (kg/m^3). Preferably the polymer has a density of 880 - 900 kg/m^3 , more preferably of 880 - 895 kg/m^3 .

15 The olefinic polymer (B) preferably has a melt peak temperature as measured by DSC of at most 110 °C, more preferably at most 105 °C. Still more preferably the olefinic polymer (B) has a melt peak temperature as measured by DSC between 50 - 105 °C, even more preferably between 60 - 95 °C, most preferably between 65 and 88 °C . The degree of crystallinity, as measured by DSC, preferably is <25 , more preferably < 20%, most preferably < 15%

20 Preferably the olefinic polymer (B) is produced by a single site catalyst, most preferably by a metallocene catalyst. Examples of suitable metallocene catalysts for the production of the olefinic polymer include compounds according to formula II:



25 In formula II, M is a transition metal selected from group IVB of the periodic table, specifically zirconium, titanium or hafnium, and L is a ligand coordinated to the transition metal. At least one ligand L is having a cyclopentadienyl skeleton.

30 As the single site catalyst, especially the metallocene catalyst, readily incorporates monomeric units of the α -olefin with the monomeric units of ethylene in the olefinic polymer (B), the monomeric units of the α -olefin are uniformly and randomly distributed along the polymer chain of the olefinic polymer (B), as opposed to conventional olefinic copolymers. For this reason the olefinic polymer (B) produced by these catalysts tend to show a narrow molecular weight distribution and a narrow melting temperature range.

If a polymer (B) is used that is produced by a single site catalyst, especially a metallocene catalyst, an even higher strain release is obtained in the shaped object.

5 The preferred olefinic polymers (B) are marketed under the tradename Exact by DSM and Engage by DOW-Dupont.

The amount of olefinic polymer (B) in the composition according to the invention may be 1 to 50 parts by weight to every 100 parts by weight of elastomeric polymer (A), preferably 5 to 45 parts by weight, more preferably 10 - 40 parts by weight, most preferably 14 - 35 parts by weight.

10 Besides the elastomeric polymer (A) and the olefinic polymer (B) the composition according to the invention may comprise usual additives. The composition may comprise carbon black in an amount of 20 - 400, preferably 40 - 200 parts by weight relative to 100 parts by weight elastomeric polymer. Also alternative reinforcement agents like silica may be used.

15 The composition may comprise one or more extenders, for example in an amount of 10 to 300 parts by weight, preferably 20 - 100 parts by weight, more preferably 40 - 80 parts by weight relative to 100 parts by weight of the elastomeric polymer. Examples of extenders are calcium carbonate and clay.

20 The composition may comprise an oil in an amount of for example 20 - 200, preferably 50 - 150 parts, relative to 100 parts by weight of elastomeric polymer.

Examples of useful oils are mineral oils, such as for example paraffinic oil and naphtenic oil or synthetic hydrocarbon oil.

25 Furthermore the composition may comprise one or more vulcanization agents. For example a sulphur based vulcanization agent in combination with an accelerator is used. It is also possible to use a peroxide based vulcanization system.

It is possible that the composition comprises further usual additives such as for example heat stabilizers, antistatic agents, antioxidants, colorants and lubricants.

30 The invention also relates to a preblend, preferably in the form of a rubber bale or a granulate comprising elastomeric polymer (A) and olefinic polymer (B).

35 The preblend is easy to transport and to dose, so is in a very suitable form to be fed to a kneading device, next to further constituents, for producing the compound that is finally shaped and vulcanised. Preferably the preblend is in the form of a granulate. The preblend makes automatic feeding to the kneading device possible, especially if it is in the form of a granulate. For good anti-sticking properties to facilitate

the dosing and transporting in the preblend the sum of elastomeric polymer (A) and olefinic polymer (B) preferably adds up to at least 75 weight %, more preferably at least 90 weight %, still more preferably 95 weight %, still more preferably 98 weight % still more preferably 99 weight %, still more preferably 99.5 weight %. Other constituents 5 next to elastomeric polymer (A) and olefinic polymer (B) for example are fillers, for example carbon black.

The invention also relates to a compounding process, in which the preblend is mixed and kneaded with further additives to produce compositions according to the invention. As mixing equipment it is possible to use a batch mixer, like 10 for example a Banbury™ mixer or a continuous mixer, for example a ZSK™ double screw extruder. Thereafter the composition usually is roll milled at moderate temperature for mastification of the elastomeric polymer. The preblend is not only very usefull, as it is easy to dose and to transport, but it also provides products, like profiles and hoses, having very good mechanical properties and resistance to weather and 15 chemical environments at a moderate price.

The invention also relates to the use of the composition according to the invention in an extrusion process, especially in an extrusion process for the production of a profile or a hose. Examples of profiles are profiles for sealing doors and windows of automobiles and buildings.

20 Very good results are obtained if the composition is used in a process in which to the extrudate a stress is applied, for example by the take off equipment of the extrusion line. Caused by the stress applied the extrudate is strained. After the stress is released the strain releases relatively fast, so that the extrudate takes its original shape.

25 Especially very good results are obtained if the stress is applied at a temperature between 20 - 100 °C, preferably 40 - 80 °C.

CLAIMS

1. Polymer composition comprising:
100 parts by weight elastomeric polymer (A), comprising monomeric units of
5 ethylene and an α -olefin,
1-50 parts by weight olefinic polymer (B), comprising :
b1. 98 - 65 weight % monomeric units of ethylene
b2. 2 - 35 weight % monomeric units of an alpha-olefin having 4 - 12 carbon
atoms,
10 polymer B having a density of 880 - 915 kg/m³,
2. Polymer composition according to claim 1, characterized in that as the
elastomeric polymer (A) a polymer is used comprising monomeric units of
ethene, an α -olefin and a non-conjugated polyene (EPDM).
3. Polymer composition according to any one of claim 1 and 2, characterized that
15 a polymer (A) is used having a crystallinity of at most 5 %.
4. Polymer composition according to any one of claims 2 or 3, charcterized in
that a polymer (A) is used comprising monomer units of a) ethylene, b) an α -
olefin, c) a non-conjugated polyene (C) which in the molecule contains one
C=C bond that is polymerizable using a Ziegler-Natta catalyst, and d)
20 optionally a non-conjugated polyene (D) which in the molecule contains two or
more C=C bonds, that are polymerizable using a Ziegler-Natta catalyst, which
polymer (A) is obtainable by a process wherein it is polymerized by means of
a catalyst composition comprising a Group 3, 4, 5 or 6 transition metal
compound and a Group 1, 2, 12 or 13 organometallic compound and a
25 compound represented by the formula:



where:

X = a halogen atom,

35 Y = H, an alkyl group with 1-30 C atoms, an aromatic group with 6-30 C-
atoms, or a halogen atom,

Z = O (oxygen) or N (nitrogen),

R independently represents H, an alkyl group with 1-30 C atoms or an aromatic group with 6-30 C atoms,

Ar = an aromatic group with 6-30 C atoms

m = 1 or 2.

- 5 5. Polymer composition according to any one of claims 1 - 4, characterized in that olefinic polymer (B) has a density of 880 - 915 kg/m³.
- 6. Polymer composition according to any one of claims 1 -5, characterized in that olefinic polymer (B) has a density of 880 - 895 kg/m³.
- 7. Polymer composition according to any one of claims 1 - 6, characterized in that olefinic polymer (B) is produced by a single site catalyst, preferably a metallocene catalyst.
- 10 8. Preblend comprising:
 - 100 parts by weight elastomeric polymer (A) and
 - 1-50 parts by weight olefinic polymer (B).
- 15 9. Preblend according to claim 8 in the form of a rubber bale or granulate.
- 10 10. Preblend according to any one of claims 8 or 9, characterized in that the sum of elastomeric polymer (A) and olefinic polymer (B) in the preblend at least adds up to 75 weight %..
- 11. A compounding process using the preblend of claim 10.
- 20 12. An extrusion process using the polymer composition as defined in any one of claims 1 - 7.

ABSTRACT.

Polymer composition comprising:

- 5 100 parts by weight elastomeric polymer (A), comprising monomeric units of ethylene and an α -olefin,
 - 1-50 parts by weight olefinic polymer (B), comprising :
 - b1. 98 - 65 weight % monomeric units of ethylene
 - b2. 2 - 35 weight % monomeric units of an alpha-olefin having 4 - 12 carbon atoms,
 - 10 polymer B having a density of 880 - 915 kg/m³,
- The composition shows a good strain release.